PB89-189849

Paint Coatings
Controlled Field and Chamber Experiments

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Apr 89

U.S. Department of Commerce
National Technical Information Service
NTIS

PB89-189849

EPA/600/3/89/032
April 1989

PAINT COATINGS: CONTROLLED FIELD AND CHAMBER EXPERIMENTS

by

Edward O. Edney

Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Project Officer

John W. Spence
Chemical Processes and Characterization Division
Atmospheric Research and Exposure Assessment Laboratory
Research Triangle Park, North Carolina 27711

ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-89/032	2.
3. RECIPIENT'S ACCESSION NO. PB89 189849/AS	
4. TITLE AND SUBTITLE: PAINT COATINGS: CONTROLLED FIELD AND CHAMBER EXPERIMENTS	5. REPORT DATE: April 1989
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): E. O. Edney	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Atmospheric Research & Exposure Assessment Lab Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. N104/G/06/6121 Fy-89 11. CONTRACT/GRANT NO. In house
12. SPONSORING AGENCY NAME AND ADDRESS: Atmospheric Research & Exposure Assessment Lab Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

To determine the impact of pollution levels on the weathering rates of coatings, laboratory chamber experiments and controlled field exposures at North Carolina and Ohio sites were conducted in such a manner to separate the contributions due to dry deposition, wet deposition, precipitation pH, etc. The results of these studies confirm that acidic gases such as SO_2 and HNO_3, as well as acids within rain, promote the dissolution of alkaline components including $CaCO_3$, ZnO, and Al flake from paint films. It is unclear from these studies whether the removal of these components reduces the service life or protective properties of the paint film. Other researchers within the Coatings Effects Program are conducting subsequent analyses to determine micro-damage of these paints. The uptake of acidic gases to painted surfaces is a complex process that depends on several factors. The deposition rate of SO_2 to a wet, painted surface may be controlled by the level of oxidants such as H_2O_2.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report): UNCLASSIFIED	21. NO. OF PAGES: 20
	20. SECURITY CLASS (This page): UNCLASSIFIED	22. PRICE: A03/13.95/06.95 MF

EPA Form 2220-1 (9-73)

DISCLAIMER

This document is an internal report that has been reviewed in accordance with U.S. Environmental Protection Agency guidance and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

To determine the impact of pollution levels on the weathering rates of coatings, laboratory chamber experiments and controlled field exposures at North Carolina and Ohio sites were conducted in such a manner to separate the contributions due to dry deposition, wet deposition, precipitation pH, etc. The results of these studies confirm that acidic gases such as SO_2 and HNO_3, as well as acids within rain, promote the dissolution of alkaline components including $CaCO_3$, ZnO, and Al flake from paint films. It is unclear from these studies whether the removal of these components reduces the service life or protective properties of the paint film. Other researchers within the Coatings Effects Program are conducting subsequent analyses to determine micro-damage of these paints. The uptake of acidic gases to painted surfaces is a complex process that depends on several factors. The deposition rate of SO_2 to a wet, painted surface may be controlled by the level of oxidants such as H_2O_2.

TABLE OF CONTENTS

SECTION		PAGE
	Abstract	iii
	List of Figures	vi
	List of Tables	vii
	Acknowledgment	viii
1	Introduction	1
2	Technical Approach	2
	Laboratory Studies	2
	Controlled Field Studies	3
3	Results	6
4	Discussion	9
5	Conclusions	10
	References	11

LIST OF FIGURES

FIGURE		PAGE
1	Laboratory Exposure System	2
2	Schematic of North Carolina Covering/Spray System	3
3	$SO_4^=$ Runoff Concentration as a Function of SO_2	7

LIST OF TABLES

TABLE		PAGE
1	Accumulated Runoff Concentration for Laboratory Incremental SO_2 Experiments	6
2	North Carolina Average Runoff Rates for Selected Compounds	7
3	Ohio Average Rates for Selected Compounds	8

ACKNOWLEDGMENT

The author wishes to recognize Susan F. Cheek and Eric W. Corse with NSI Technology Services Corporation for their effort in acquiring laboratory and field exposure data of the coatings. These results were essential to the development of this report.

SECTION 1

INTRODUCTION

Because of the high volume of paint used in the United States, any decrease in service life by pollution effects could result in significant economic loss. Determining the impact of pollution levels on weathering rates requires the development of models that relate the amount of damage to environmental factors. The construction of such models requires understanding: (1) the wet and dry deposition of pollutants to painted surfaces, (2) interactions between deposited compounds and interactions of these species with components of the paint film and the substrate, and (3) the relationships between reactions on a molecular scale and macroscopic damage. To address some of these issues we have developed laboratory and field systems capable of exposing materials to complex air mixtures but in a manner such that the separate contributions due to dry deposition, wet deposition, precipitation pH, etc., can be evaluated.

PROJECT OBJECTIVES

1. To conduct controlled laboratory experiments to determine the components of a typical urban smog mixture that deposit to painted surfaces in the absence and presence of surface moisture.

2. To conduct controlled field studies to determine the separate effects of dry deposition, wet deposition, and precipitation pH on the damage rates of paint under ambient conditions.

SECTION 2

TECHNICAL APPROACH

LABORATORY STUDIES

Laboratory studies were conducted using the exposure system shown in Figure 1. The system consists of two parallel exposure chambers and a smog chamber that is operated as a continuously stirred tank reactor and serves as a reservoir for the exposure chambers. The flow rate through the 11.3-m^3 smog chamber is 100 Lpm, whereas turbulent conditions are generated in the exposure chambers by circulating air through the 26-L chambers at a flow rate of 2500 Lpm. Each exposure chamber has a chiller back plate that can be chilled below the air dew-point to generate dew that, if produced in a sufficient quantity, can be collected and analyzed. The air dew-point is regulated using a computer-controlled steam system. Hydrocarbon concentrations are measured using gas chromatography; and NO_X, NO, O_3, and SO_2 levels are determined using commercial instruments. Gas-phase and particulate NO_3^-, as well as $SO_4^=$ concentrations, are measured by ion chromatography. The dew samples are analyzed using the technique described below for runoff analysis.

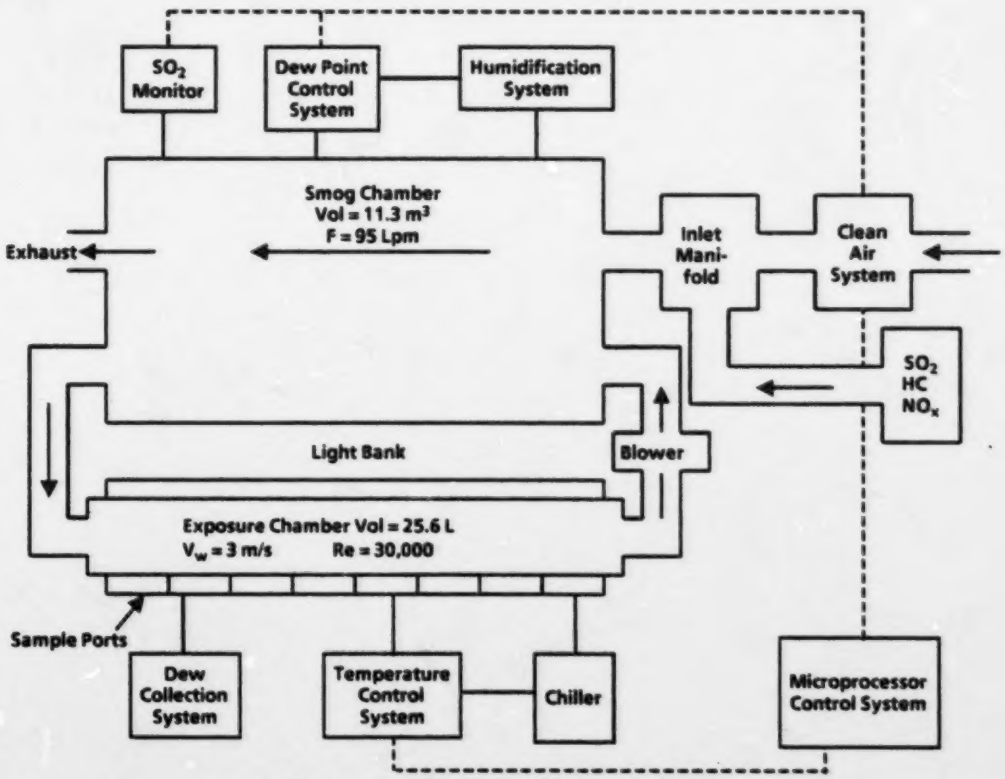

Figure 1. Laboratory Exposure System.

CONTROLLED FIELD STUDIES

To separate the effects of dry and wet deposition on weathering of paints, covering/spray systems were designed and installed in Research Triangle Park, NC, a relatively unpolluted site, and in Steubenville, OH, a site with high levels of SO_2. The automated systems are used to expose materials under the following conditions: (1) dry deposition only, (2) dry plus ambient wet deposition, and (3) dry deposition plus deionized water (DI). Each system consists of movable and stationary racks, a shelter, moisture-sensing information, and a DI-spray system. A schematic of the North Carolina system is shown in Figure 2.

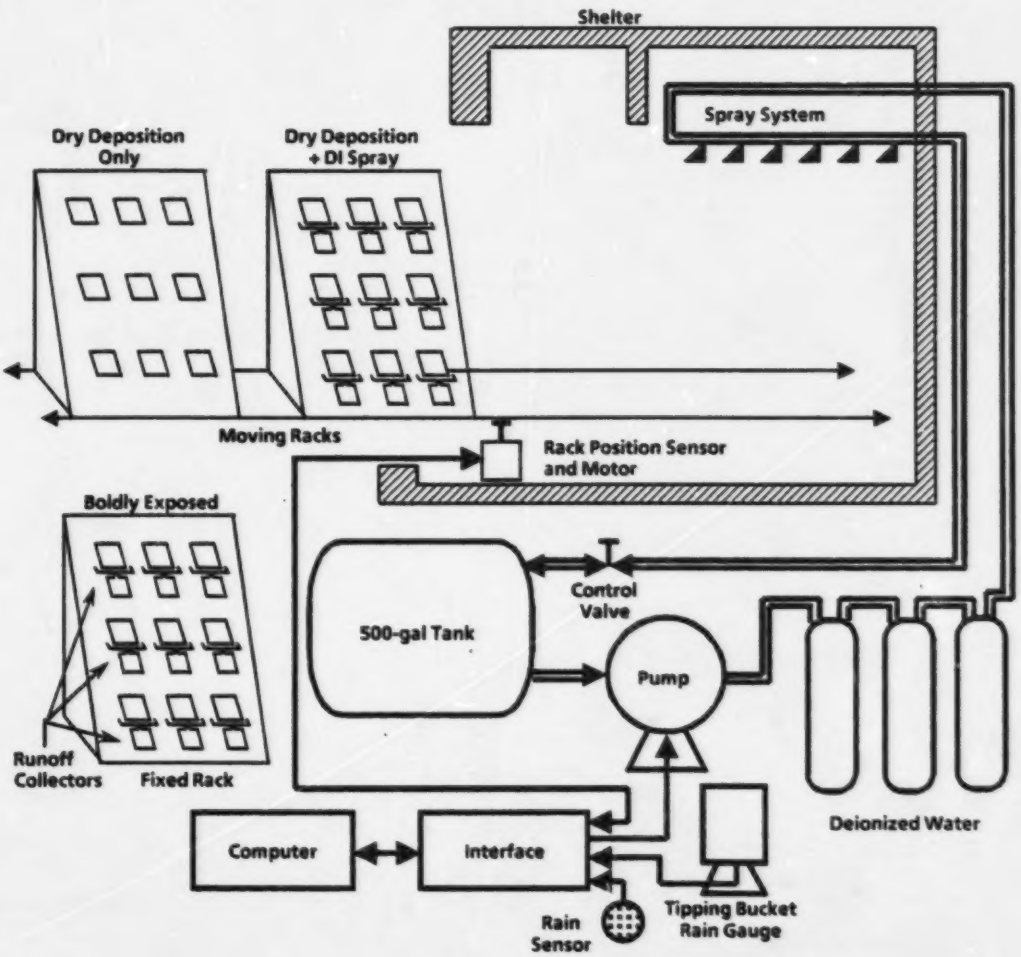

Figure 2. Schematic of North Carolina Covering/Spray System.

At the onset of precipitation, the movable racks automatically are brought under the shelter to avoid ambient precipitation. The racks remain inside as long as the moisture sensor is wet. Once the sensor dries, the racks are returned to the ambient-exposure condition. The operation of the DI-spray system at the Ohio site differs from that at the North Carolina site. The North Carolina system is computer-controlled and the test panels, located under the sheltered spray system, automatically are sprayed for a fixed period of time (~50 s for each 0.13 cm of ambient precipitation that accumulates in the exposed tipping bucket). At the Ohio site, the panels are sprayed after the completion of the precipitation event.

At each site, runoff collectors are located at some of the test-panel positions. Runoff samples are collected on an event basis and undergo detailed chemical analyses. Each runoff sample is analyzed for Na^+, NH_4^+, K^+, $HCOO^-$, Cl^-, NO_3^-, $HSO_3^-/SO_3^=$, and $SO_4^=$ by ion chromatography and for Zn and Ca by atomic absorption spectroscopy. In addition, the volume and pH of each sample are determined.

For both the runoff and laboratory experiments, it is convenient to express the aqueous concentrations in terms of runoff concentrations R_i and runoff rates F_i, that is,

$$R_i = \frac{[X]_i V_i}{A} \tag{1}$$

$$F_i = \frac{R_i}{t_i} \tag{2}$$

$$R = \sum_{i=1}^{N} R_i \tag{3}$$

$$F = \frac{R}{t} \tag{4}$$

where i denotes the precipitation or dew event; t_i is the exposure time for the i^{th} event; V_i is the aqueous volume collected; A is the surface area; R is the accumulated runoff concentration through N events; and F is the average runoff rate.

The paints investigated included latex paints with and without $CaCO_3$ (latex and latex-c, respectively), an oil-based paint with ZnO and $CaCO_3$ (oil-cz), and a maintenance oil-based paint (oil). Each of the white paints employed TiO_2 as the pigment. For the laboratory experiments, latex, latex-c, and oil-cz were applied to galvanized steel substrates, whereas for the field studies, red cedar was used for the substrate. A steel substrate was used for the oil paint for both applications.

The laboratory experiments consisted of exposing films in the absence and presence of surface moisture to a series of irradiated $C_3H_6/NO_X/SO_2$ mixtures in air, where the only parameter varied was the SO_2 level. The objective of the experiments was to determine the impact of incremental changes in the SO_2 level on the dissolution rates of alkaline paint components. Exposure experiments were conducted for SO_2 levels of 0, 9, 18, 25, 50, 82, 134, 193, 326, 396, 534, and 722 ppb. Approximate steady-state concentrations for other compounds were O_3, 230 ppb; NO_X, 180 ppb; HCHO, 380 ppb; and HNO_3, 7 ppb. Each experiment consisted of a 21-h exposure where thin films of moisture were generated during the last 4 h in one of the chambers. Another set of panels remained dry throughout the exposure. At the completion of each experimental run, both the dry and dew panels were rinsed with 10 mL of DI and the rinse was analyzed chemically.

The North Carolina paint field exposure experiment began March 15, 1988, and the results reported here cover the time period through November 6, 1988. The exposure results at the Ohio site cover the time period between July 25, 1988, and October 25, 1988.

SECTION 3

RESULTS

The accumulated runoff concentrations for selected compounds for the entire sequence of laboratory SO_2-exposure experiments are shown in Table 1. Results of the analysis of the runoff from galvanized steel panels also are included in Table 1 for comparative purposes. Figure 3 shows the $SO_4^=$ runoff concentration for dew panels as a function of SO_2 concentration. The DI-spray and ambient runoff rates for the North Carolina and Ohio field studies are presented in Tables 2 and 3.

TABLE 1. ACCUMULATED RUNOFF CONCENTRATION FOR LABORATORY INCREMENTAL SO_2 EXPERIMENTS R(nmole/cm²)

Sample	Condition	Vol-m[a]	H^+	Ca	Zn	$HCOO^-$	NO_3^-	HSO_3^-	$SO_4^=$	HCHO
Latex	Dew	1.89	4.6	2.4	74.9	47.5	108.3	12.7	32.5	53.7
Latex	Dry	0.00	18.2	2.6	31.6	2.3	129.8	0.0	4.8	ND[b]
Latex-c	Dew	2.06	13.8	357.0	59.6	123.6	161.1	368.6	86.8	533.6
Latex-c	Dry	0.00	3.0	255.5	30.8	7.0	497.8	0.0	7.3	ND
Oil	Dew	1.57	144.4	3.2	37.2	55.2	120.1	0.0	96.8	164.9
Oil	Dry	0.00	4.9	0.8	9.4	2.7	22.6	0.0	4.4	ND
Oil-cz	Dew	4.26	38.6	109.6	171.2	105.7	306.6	13.4	100.7	249.7
Oil-cz	Dry	0.00	4.3	40.6	50.0	4.0	147.2	0.0	5.2	ND
G-steel[c]	Dew	5.99	21.2	1.7	2277.6	704.1	517.2	2235.6	692.0	3668.1
G-steel	Dry	0.00	2.1	0.9	425.3	7.7	764.1	0.0	46.1	ND

[a] Total volume of dew collected.
[b] No data.
[c] Galvanized steel.

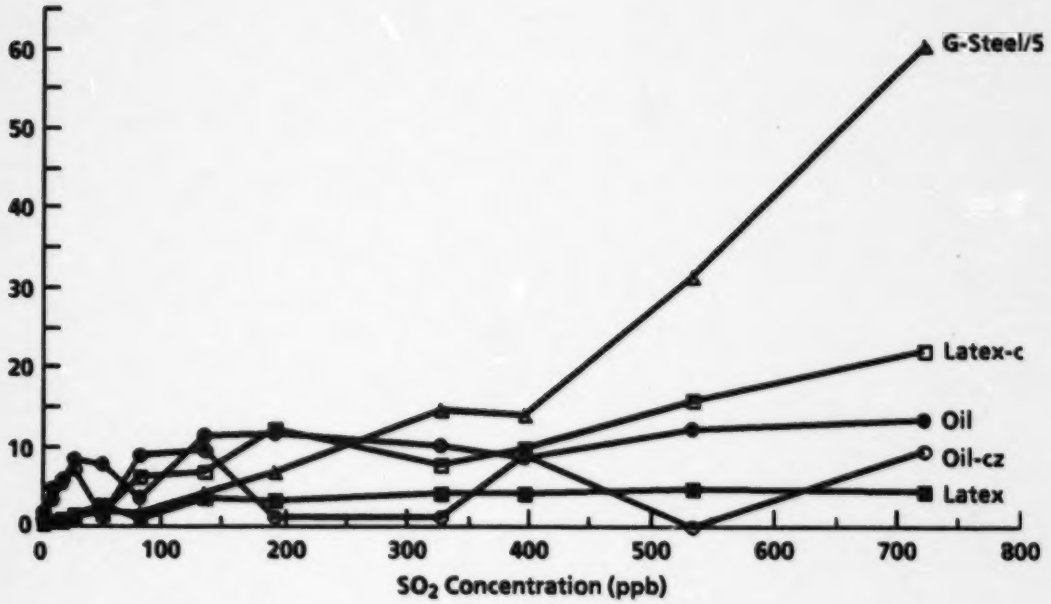

Figure 3. $SO_4^=$ Runoff Concentration as a Function of SO_2.

TABLE 2. NORTH CAROLINA AVERAGE RUNOFF RATES FOR SELECTED COMPOUNDS
R(nmole/cm²-day)

Sample	Condition	H^+	Na^+	K^+	Ca	Zn	$HCOO^-$	Cl^-	NO_3^-	$SO_4^=$
Latex	DI	0.28	2.09	1.14	0.59	ND	0.24	0.35	1.22	1.22
Latex	Ambient	4.18	3.02	1.78	2.12	ND	0.98	7.29	5.73	5.17
Latex-c	DI	0.13	1.67	0.74	4.25	ND	0.29	4.36	1.80	1.46
Latex-c	Ambient	1.29	3.36	2.11	11.75	ND	0.94	10.17	6.91	6.45
Oil	DI	0.49	0.44	0.27	0.63	ND	0.06	1.01	0.79	0.59
Oil	Ambient	4.16	0.85	0.93	0.83	ND	0.46	1.68	2.22	2.70
Oil-cz	DI	0.88	0.35	0.87	1.19	0.64	1.42	1.23	1.04	0.52
Oil-cz	Ambient	1.32	0.69	0.34	3.63	1.98	0.44	2.70	4.19	3.37

TABLE 3. OHIO AVERAGE RUNOFF RATES FOR SELECTED COMPOUNDS
R(nmole/cm²-day)

Sample	Condition	H^+	Na^+	K^+	Ca	Zn	$HCOO^-$	Cl^-	NO_3^-	$SO_4^=$
Latex	DI	0.10	3.43	0.73	5.18	ND	1.41	6.38	1.06	4.22
Latex	Ambient	5.40	0.78	0.90	15.15	ND	0.07	6.67	11.02	19.15
Latex-c	DI	0.08	4.23	0.85	6.94	ND	1.47	6.36	1.22	4.73
Latex-c	Ambient	1.91	0.85	1.03	24.14	ND	0.07	8.50	13.01	24.31
Oil	DI	0.25	5.11	0.68	3.36	ND	1.78	7.42	0.80	3.34
Oil	Ambient	3.50	0.60	0.69	13.69	ND	0.07	4.55	9.60	15.38
Oil-cz	DI	0.14	2.42	0.33	3.24	0.99	1.17	4.36	0.76	2.90
Oil-cz	Ambient	1.59	0.87	0.76	19.96	3.47	0.09	5.47	11.46	20.50

SECTION 4

DISCUSSION

The laboratory runoff results show the dew samples consisted of complex mixtures of ions whose composition depended upon both the reactivity of the material and the moisture condition. The deposition of acid gases such as HNO_3 and SO_2 led to the dissolution of $CaCO_3$ in latex-c, ZnO and $CaCO_3$ in oil-cz, and to Zn corrosion productions on galvanized steel. The presence of Zn in the latex-c and latex samples suggests that Zn from the substrate was leached through the latex paints. The dominant cation in the oil paint runoff was H^+, a result consistent with the lack of alkaline compounds in the paint. The effect of surface moisture on NO_3^- precursors (e.g., HNO_3) was dependent on the composition of the coating. The uptakes of NO_3^- precursors in complex air mixtures to dry panels were larger for latex, latex-c, and galvanized steel than for the dew panels, whereas the situation was reversed for oil and oil-cz. The uptake of SO_2 appears to be a function of surface reactivity: The largest deposition took place on galvanized steel, while the lowest value occurred for oil.

Figure 3 suggests that the uptakes of SO_2 to moisture-covered, relatively inert surfaces such as oil, oil-cz, or latex were not directly proportional to the SO_2 level. The uptakes may have been controlled by the level of available oxidants such as H_2O_2, a situation similar to that controlling the acidification of cloud water. However, for more alkaline surfaces such as latex-c and, in particular, galvanized steel, the absorption rate is proportional to the SO_2 level.

The North Carolina and Ohio runoff results are consistent with the laboratory results in that the dry and wet deposition of acid gases dissolves $CaCO_3$ in latex-c and oil-cz and Zn compounds in oil-cz and galvanized steel. In general, the amounts dissolved at the Ohio site were larger than the corresponding values in North Carolina, a result qualitatively consistent with the higher pollution levels in Ohio. The presence of large amounts of Ca in the Ohio samples raises the question as to whether neutralization of acid gases by dry-deposited alkaline particles occurred in Ohio.

SECTION 5

CONCLUSIONS

The following conclusions are based on results reported here and those that have been previously reported in the literature.

1. Laboratory experiments suggest and field studies confirm that dry deposition of acid gases such as SO_2 and HNO_3 dissolve alkaline compounds in paint films. Field studies also show that wet-deposited acids in precipitation produce additional dissolution. Alkaline compounds susceptible to acidic deposition include $CaCO_3$, ZnO, and Al compounds in aluminum flake paints.

2. The uptake of acid gases to painted surfaces is a complex process that depends upon the moisture condition, surface reactivity, permeability of the coating, and reactions with other compounds deposited on the surface. Those painted surfaces that react readily with deposited acids tend to more readily absorb these atmospheric acids than the more inert surfaces.

3. Laboratory and field studies suggest that factors other than just the SO_2 level are important in determining the deposition rates of SO_2 to wet, painted surfaces. The levels of oxidants such as H_2O_2 could be a controlling factor in the deposition process.

4. The leaching of ZnO, a mildewcide, is a form of damage, but it is not clear that removal of extenders such as $CaCO_3$ constitutes a process that reduces the paint service life. The most significant pollution-induced effect may be those processes whereby gaseous pollutants are absorbed into the film and alter polymer oxidation processes, possibly changing the protective properties.

REFERENCES

1. Edney, E.O., S.F. Cheek, D.C. Stiles, E.W. Corse, M.L. Wheeler, J.W. Spence, F.H. Haynie, and W.E. Wilson. 1988. Effects of acid deposition on paints and metals: Results of a controlled field study. *Atmos. Environ.* 22: 2263-2274.

2. Edney, E.O., E.W. Corse, S.F. Cheek, W.E. Wilson, J.W. Spence, and F.H. Haynie. 1988. Impact of oxidants on the uptake of complex air mixtures to material surfaces. *Extended Abstracts of Papers.* Los Angeles, CA: The 196th ACS National Meeting 28(2):126-128.

3. Edney, E.O., S.F. Cheek, E.W. Corse, J.W. Spence, and F.H. Haynie. Submitted. Atmospheric weathering caused by dry deposition of acidic compounds. *J. Environ. Sci. and Health A.*

4. Edney, E.O., E.W. Corse, S.F. Cheek, J.W. Spence, and F.H. Haynie. Submitted. Uptake of components of an irradiated $C_3H_6/NO_X/SO_2$/air mixture to material surfaces in the absence and presence of moisture. *Atmos. Environ.*